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KIRK-OTHMER

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EXPLOSIVES AND PROPELLANTS
TO
FLAME RETARDANTS FOR TEXTILES

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750 FILLERS Vol. 10

tion should have similar coefficients of thermal expansion. This prevents stressinduced damage that occurs when substances expand or contract to different degrees as temperature is increased or decreased. Coefficients of thermal expansion are reported in units of dimension change per degree Celsius for a specified temperature range. Many fillers expand differently in different dimensions.

Hardness. The hardness (qv), or related property abrasiveness, is an important filler property. Hardness is determined by comparison to materials of known hardness on the Mohs' scale. On this nonlinear scale, diamond is rated 10, quartz 7, calcite 3, and talc 1. The abrasiveness of a filler is also dependent on psd and the presence of impurities, eg, kaolin clay (Mohs' hardness of 3) can be quite abrasive because of the presence of quartz impurities.

## Filled Polymer Systems

Polymer systems have been classified according to glass-transition temperature  $(T_g)$ , melting point  $(T_m)$ , and polymer molecular weight (12) as elastomers, plastics, and fibers. Fillers play an important role as reinforcement for elastomers. They are used extensively in all subclasses of plastics, ie, general-purpose, specialty, and engineering plastics (qv). Fillers are not, however, a significant factor in fibers (qv).

Elastomers. In the rubber industry the terms filler, reinforcement, and pigment have been used for the same material, derived from different sources. Most rubber technologists distinguish inert fillers from reinforcing fillers. Inert fillers, such as clay, improve the workability of the unvulcanized rubber stock but have little effect on the final properties; reinforcing fillers improve the mechanical properties of the vulcanized rubber. In practice, these materials impart abrasion resistance, tear resistance, tensile strength, and stiffness. The reinforcing action of a given material is primarily dependent on its chemical composition and the type of elastomer in which it is compounded. For instance, carbon black in isoprene rubber and pyrogenic silica in silicone rubbers are more active reinforcing agents in these respective elastomers than other fillers with equivalent particle size distributions. In general, as particle size diminishes or surface condition improves, most fillers become more reinforcing. Table I lists typical elastomer fillers and their uses.

Since most fabricated elastomer products contain 10–50 vol % of filler, their physical properties and processing characteristics depend to a great extent on the nature and quality of the fillers. Rubber technologists manipulate the formula so as to optimize a large number of properties and keep costs down.

Recovery, Rebound, or Nerve. Uncured latex stock tends to recover its previous shape after being rolled or extruded during processing. This tendency can result in processing difficulties and reduces dimensional accuracy of the finished products. The recovery of latex stock can be reduced by adding large particle-size fillers, or fillers which possess a high degree of particle aggregation, ie, agglomerated or structured fillers such as carbon black or pyrogenic silica, or by increasing the loading of other fillers.

Tack. Tack causes layers to adhere when they are pressed together. This property can be reduced by employing fillers with a finer psd or by dusting the

Table 1. Elastomer Fillers

Filler	Specific gravity	Compatible elastomer <sup>a</sup>	Uses
alumina	2.7	NR, CR, SRs	hose, mats
asbestos	2.4	NR, SRs	mats, tile
barium sulfate	4.3	NR, CR, SRs	O-rings, belts
carbon blacks <sup>b</sup>	1-2.3		<b>G</b> ,
N110		IR, NR	tires, pads
N220		NR, SBR	tire treads
N550		NR, SRs	extruded goods tubes footwear
N660		BR, NR	
N762		NR, SRs	
N774		NR, SRs	tire carcasses
N990		CR, EPDM	extruded goods
calcium carbonate	2.7 - 2.9	NR, SRs	footwear, mats
kaolin clay	2.6	NR, SBR, EPM, EPDM	flooring, footwear
mica	2.8	NR, SRs	molded goods
resins	1.2	NBR, CR, NR, SBR	footwear, coatings
silicas			
colloidal	1.3	NR, SBR	sponge carpet backing molded goods hygienic goods
diatomaceous	2.2	NR, IIR	
novaculite	2.7	NR, SRs	
wet process	2	IIR, CR, NBR, NR	
pyrogenic	2.2	silicone rubber	electrical goods
surface treated		NR, SRs	specialty goods
talc	2.8	NR, CR, IIR, EPM	molded goods
natural materials <sup>c</sup>	1.1	NR, SBR, CR	tape, extruded goods
wood and shell flour	0.9 - 1.6	CR, NR, SRs	footwear

<sup>&</sup>lt;sup>a</sup>NR, natural rubber; CR, chloroprene; SRs, synthetic rubbers; IR, natural isoprene; SBR, styrene-butadiene rubber; BR, butadiene; EPDM, ethylene-propylene-diene; EPM, ethylene-propylene polymer; IIR, isobutylene-isoprene; NBR, nitrile-butadiene.

stock with a laminar filler such as mica. In a related value, fillers such as mica can inhibit adhesion to the mold during processing.

Retardation (Scorch Resistance). Scorch is the premature vulcanization of an elastomer during processing. The tendency of an elastomer to scorch can be reduced by compounding it with a filler of different acidity or larger particle size. The type of filler also affects the tendency of a latex stock to scorch, ie, highly reinforcing fillers such as carbon black, silica, and zinc oxide promote scorching, whereas most clay fillers retard scorching.

Abrasion Resistance. The tendency of rubber to undergo surface attrition when subjected to frictional force is called abrasion. The abrasion resistance of a given rubber is a function of both filler type and form. If listed in order of their decreasing effectiveness in preventing abrasion, carbon black > silica > zinc oxide > clay > calcium carbonate. Although the abrasion resistance of fillers tends to

(4/7)

<sup>&</sup>lt;sup>b</sup>Carbon black grades identified by four characters (ASTM D1765-67), ie, cure rate of normal (N) or slow (S), digit classifying typical particle size in nm, and two arbitrarily assigned characters. <sup>c</sup>For example, rice.

752 FILLERS Vol. 10

increase with increasing sphericity and decreasing particle size, fillers should be compared by evaluating their abrasion resistance using samples prepared at equal loading and by a procedure such as ASTM method D1630.

Elongation. The extension produced by a tensile stress applied to an elastomer, ie, elongation, is almost always reduced by fillers. Regardless of what type of filler is used, elongation decreases with increased loading above approximately 5 vol % (13).

Hardness. The resistance of a fabricated rubber article to indentation, ie, hardness, is influenced by the amount and shape of its fillers. High loadings increase hardness. Fillers in the form of platelets or flakes, such as clays or mica, impart greater hardness to elastomers than other particle shapes at equivalent loadings.

Modulus of Elasticity (Stiffness). The stress-strain behavior of a material under tension is an important characteristic. The slope of the stress vs strain curve is called the modulus of elasticity or stiffness. Reinforcing fillers result in higher modulus composites than inert fillers at equal loading. In general, modulus increases with decreasing particle size of a filler. Air voids introduced during processing, possibly as a result of filler agglomeration, can lower modulus.

Permanent Set. When an elastomer is stretched and then allowed to relax, it will not completely recover its original dimensions. This divergence from its original form is called its permanent set. It is principally affected by the affinity of the elastomer for the filler surface and is, therefore, primarily a function of the surface energy or wetting of the filler.

Resilience. The ratio of energy output to energy input in a rapid full recovery of a deformed elastomer specimen is termed resilience. It is a reliable index to the energy lost through internal friction of viscous flow. In general, fillers with the least effect on resilience are those that are least reinforcing. Zinc oxide is an exception because it has good resilience and also gives good reinforcement.

Tear Resistance. The resistance of an elastomer to tearing is affected by the particle size and shape of the filler it contains. Tear resistance generally increases with decreasing particle size and increasing sphericity of fillers.

Tensile Strength. Fillers of small particle size and large surface area increase the tensile strength of a rubber compound. For most fillers, tensile strength increases with loading to an optimum value after which it decreases with increased loading.

**Plastics.** In the plastics industry, the term filler refers to particulate materials that are added to plastic resins in relatively large, ie, over 5%, volume loadings. Except in certain specialty or engineering plastics applications, plastics compounders tend to formulate with the objective of optimizing properties at minimum cost rather than maximizing properties at optimum cost. Table 2 lists typical plastic fillers and their uses.

Resin Viscosity. The flow properties of uncured compounded plastics is affected by the particle loading, shape, and degree of dispersion. Flow decreases with increased sphericity and degree of dispersion, but increases with increased loading. Fillers with active surfaces can provide thixotropy to filled materials by forming internal network structures which hold the polymers at low stress.

Resin Curing. Fillers with high surface areas can retard the curing of plastics by adsorbing catalysts or promoters. Other fillers can accelerate curing if they

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Table 2. Plastic Fillers and Their Primary Functions

Filler	Specific gravity	Compatible resins <sup>a</sup>	Primary function
alumina trihydrate carbon blacks	2.42 . $1-2.3$	varied varied	flame retardance optical, electrical, mechanical
calcium carbonate			
mineral	2.60 - 2.75	PVC, HDPE	multiple, cost
synthetic	2.7	rigid PVC, PP	impact, weathering
kaolin	2.58-2.63	varied	bloom prevention,
feldspar	2.61	ABS, EVA, SMC	translucency
organics			•
wood flour	0.65	varied	reinforcement
starch	1.5	varied	biodegradability
silicas, synthetic			
fumed silica	2.2	FRP, PVC, epoxy	rheology
silica gel		PVC, LDPE	gloss reduction
precipitated silica	1.9 - 2.2	PVC, PE, EVA	thixotropy
fused silica	2.18	general	electrical
silicas, natural			
crystalline silicas	2.65	general	mechanical, cost
diatomaceous silica	2.65	LDPE fims	antiblocking
sphericals			-
hollow glass	0.15 - 0.30	PVC, SMC, BMC	weight reduction
fly ash	0.30 - 1.0	varied	cost reduction
solid glass ,	2.5	varied	mechanical
talcs	2.7–2.8	PP, HDPE, TPE, PVC	reinforcement

<sup>&</sup>quot;HDPE, high density polyethylene; PP, polypropylene; EVA, ethylene-vinyl alcohol; SMC, sheet-molding compound; FRP, fiber-reinforced plastic; LDPE, low density polyethylene; PE, polyethylene; BMC, bulk molding compound; TPE, thermoplastic elastomer.

contain active sites or trace quantities of catalytic materials. Low density fillers cause high temperatures during curing and subsequent long cool-down periods because of their insulating effects. High loadings of dense solid fillers can appreciably increase the curing time needed to fully cure thermosetting compounds.

Tensile Strength. The tensile strength of filled plastic compositions is affected by filler particle shape and size, psd, surface area, and interfacial bonding. In general, tensile strength increases with decreasing sphericity of fillers. At equivalent volume loadings, small filler particle sizes and a narrow psd give better tensile strengths than large particle sizes and broad distributions. Higher filler surface areas and, in general, stronger filler-to-matrix bonding also result in higher tensile strength compositions. Tensile strength of plastics is measured by ASTM D638-76.

Compressive Strength. The strength of the weakest component of the system, be it filler, matrix, or the bond area between the filler and the matrix, governs the compressive strength of filled compositions. The weak compressive fillers,

**FILLERS** Vol. 10

such as celluloses, reduce the compressive strength of composites, whereas the reverse is true for strong, rigid fillers such as mineral oxides. Compressive strength of plastics is measured by ASTM D621-64.

Fire Resistance. Many fillers, particularly inorganic oxides, are noncombustible and provide a measure of passive fire resistance to filled plastics by reducing the volume of combustible matter in the filled composition. Depending on their density, they may also serve as insulation.

Fillers that contain combined water or carbon dioxide, such as alumina trihydrate, Mg(OH)<sub>2</sub>, or dawsonite [12011-76-6], increase fire resistance by liberating noncombustible gases when they are heated. These gases withdraw heat from the plastic and can also reduce the oxygen concentration of the air surrounding the composition.

Electrical Resistance-Conductivity. Most fillers are composed of nonconducting substances that should, therefore, provide electrical resistance properties comparable to the plastics in which they are used. However, some fillers contain adsorbed water or other conductive species that can greatly reduce their electrical resistance. Standard tests for electrical resistance of filled plastics include dielectric strength, dielectric constant, arc resistance, and d-c resistance.

## Other Filler Systems

Paper. Paper is prepared by depositing cellulose pulp fibers on a continuous wire screen from a dilute suspension in water (see PAPER). Fillers, or loading materials, are finely divided solids that are incorporated into the paper sheet structure by adding them to the pulp slurry prior to its deposition on the wire. Finely divided solids dispersed in water containing an adhesive and then coated on the paper after it has been formed are usually termed coating pigments. Here the term filler is used for both loading materials and coating pigments. Table 3 lists typical paper fillers and their uses. Most paper contains 1-40 wt % of fillers (ca 1993). The optical and mechanical properties of filled paper are superior to those of unfilled paper.

Optical Properties. Brightness, or visual whiteness of paper, can be defined as the degree to which light is reflected uniformly over the visible spectrum. Since pulp and typical impurities tend to be yellowish, blue dye is sometimes added in addition to appropriate fillers. The percentage reflectance is usually measured in the blue end of the spectrum at or near 457 nm (14).

The ability of fillers to improve paper brightness increases with their intrinsic brightness, surface area, and refractive index. According to the Mie theory, this ability is maximum at an optimum filler particle size, about 0.25 µm in most cases, where the filler particle size is roughly one-half the wavelength of light used for the observation.

Gloss, or surface luster, is the property of a surface to reflect light specularly. It is associated with such phenomema as shininess, highlight, and reflected images. The gloss of paper is usually quantified with a spectrophotometer which measures light at a variety of angles of incidence and reflection.

Paper gloss is influenced by the size and shape of filler particles at the surface of the paper. A roughness on the order of one-fourth of the wavelength of